PATENT SPECIFICATION

NO DRAWINGS

1,117,129

1,117,129

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Date of Application and filing Complete Specification: 18 September, 1965 No. 39881/65

Complete Specification Published: 19 June, 1968.

Index at Acceptance:—A5 B 34; C3 R (22C4, 22C9A, 22C9B, 22C10, 22C11, 22C12, 22C16, 22C21, 22C25, 22D1A1, 22D1AX, 22D2AX, 22L2A, 22L2X, 22L4G, 22N1A); C4 X 11.

Int. CL:—A 61 k 7/06.

COMPLETE SPECIFICATION

A Cosmetic Preparation

We, YARDLEY AND COMPANY LIMITED, a British Company of London, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to hair grooming compositions, including hair fixature compositions.

For many years compositions based on hydrocarbon oils and oil gels, such as petrolatum, have been sold for restoring oil to dry hair and scalp, to brighten the hair and to impart to it a measure of manageability. Such compositions suffer from a variety of disadvantages.

The oil gel types of hair grooming compositions, often called "pomades" or "solid brilliantines" are most used for hair control; but they have poor lubricity, and poor spreadability, and thus are likely to leave a high degree of stickiness or greasiness on the hair, which is objectionable to many persons. Such compositions made by bodying mineral oil by use of known agents such as aluminium stearate or paraffin wax, are subject to separation of liquid oil (syneresis), friability of the gel structure, shrinkage within the jar, and poor spreadability. These characteristics have made such compositions less than satisfactory and have limited their use.

The heavier oils in liquid form also are difficult to spread thinly and uniformly on the hair; whereas the thinner oils tend to run off the hands and hair and down onto one's face or neck or along one's wrist, onto sleeves or other parts of one's clothing.

The liquid oil compositions are also less than satisfactory in their grooming and fixative effects. The oil is not absorbed by the hair and, to the extent that it provides hair control, it also causes an objectionable oiliness and apparent matting, "plastering down" of the hair.

The present invention is based upon the discovery that desirable and effective hair grooming compositions can be made by at least partly dissolving polyamide material in a liquid, oily, non-polar solvent consisting of or including a substance having a chain of at least 10 carbon atoms in its molecule, the polyamide material being a reaction product of an aliphatic poly-carboxylic acid and an alkylene polyamine and having an average molecular weight between 2000 and 14000. Advantageously the polyamide material is of the type set forth in U.S. Patents Nos. 2,450,940 and 2,379,413, having an average molecular weight between 2000 and 10000 and being reaction products of aliphatic dicarboxylic acids and di- or polyamino compounds.

The present invention provides a hair grooming and hair treating composition which is free from the serious disadvantages of the prior compositions, and thus provides improvements in such compositions and in the art of hair grooming which have long been sought, but had seemed unattainable.

The composition may include a cosolvent as well as the oily vehicle (the solvent). The cosolvent dissolves the resin and is miscible with the oil so as to bring the composition into the form of a stable gel or suitably bodied or polymerized liquid. Other ingredients may be included for example, ordinary cosmetic diluents and ingredients, for example, scents and tinting colours.

These may be added to the oily vehicle non-polar materials solid at ambient temperature. The oily vehicle may include, for example, mineral oils which are advantageously of 50-70 Saybolt viscosity. Higher viscosity oils have less compatibility with

[Price 4s. 6d.]

Price 25p

Price 33p

Price 75p

the polyamide material and give less clear gels.

The cosolvents or coupling agents chosen are cosmetically acceptable compounds which form with the resin a solution which is miscible with the oily vehicle. In general, the cosolvent is a substance in which both the resin and the oil are soluble. The most advantageous liquids as cosolvents are of the class of fatty acids, alcohols and glycol esters having a hydrocarbon radical of the kind found in vegetable oils, most advantageously the hydrocarbon radical has a straight chain of 12-18 carbon atoms. Typical examples of cosolvents are oleic acid, linoleic acid, mixtures of oleic and linoleic acids, diethanolamine linoleate, oleyl alcohol, propylene glycol mono laurate, propylene glycol di-laurate, propylene glycol monomyristate, propylene glycol monooleate, lauryl lactate, myristyl lactate, methyl salicylate, castor oil, ethanol, isopropanol, di-butyl phthalate, di-butyl sebacate, and di-octyl sebacate, or mixtures thereof. However, some of the above cosolvents, for example propylene glycol mono laurate, can be used without the oily vehicle in which case they act as the oily liquid non-polar solvent.

The polyamide material as already indicated above, is advantageously a solid resinous, condensation product of an aliphatic dicarboxylic acid and a diamine (inclusive of compounds having at least one alkylene and at least two amino groups, respectively) soluble in at least some organic solvents. Suitable resins of this type are available commercially from General Mills, Inc., under the name "Versamid" (Registered Trade Mark), and from Olin-Mathison Chemical Corp., under the name "Omamid" (Registered Trade Mark), for example Omamid "S" or Omamid "C". They are tough thermoplastic resins of the polyamide type insoluble in water and in many ketones and ester solvents such as carboxylic acid amides, alcohols and chlorinated hydrocarbons, depending upon the particular acids and amines which have been used to form the resin and also upon the polymer length. Monohydric alcohols, especially those having 3-8 carbon atoms, and chlorinated hydrocarbons are generally effective and hydrocarbons and ether solvents are in some cases effective per se and in some cases effective only in mixtures with other solvents. Specifically, such solvents include n-amyl alcohol, iso amyl alcohol, benzene, iso butyl alcohol, ethyl alcohol, n-octyl alcohol, mono butyl ether of ethylene glycol, mono ethyl ether of ethylene glycol, n-propyl alcohol, iso propyl alcohol, turpentine, xylene and mixtures thereof. Chloroform, methylene chloride, turpentine and xylene, even though effective for solvent purposes, are not recommended for hair grooming cosmetics because of odour. In general, solubility is low or absent with simple hydrocarbons, but as indicated above, they may be useful in mixtures with other solvents.

Other properties of these resins appear as follows:—

	Versamid					*Omamid*	
Resin type	*900*	*930*	*940*	*950*	*100*	*C*	*S*
Specific gravity	.98	.98	.98	.98	.98	.97- .99	.94- .96
†Colour, Gardner	12	12	12	12	12	12- 14	11- 12
Melting point °C	180-190	105-115	105-115	43-55	43-55		
Softening point °C (ring and ball) Viscosity						90-100	100-120
‡Brookfield at 150°C Solid No. 2 Spindle		30-45	15-30	7-15	10-15	32- 52	55- 75
Acid value						12	12
Amine value*	3	3	3	3	83-93		

*Amine value is the weight of KOH, in milligrams, equivalent to the free amine groups in one gram of the resin.

†Gardner Colour Scale (Transparent Liquids) Ref: American Society for Testing of Materials (Standards) Part 21, 1964.

‡Brookfield viscometer data, Ref: American Society for Testing of Materials (Standards), Part 26, 1964.

"Versamid" polyamide resins are thermoplastic condensation products of polymerized linoleic acid with various polyamine compounds such as ethylene diamine, and diethylene triamine. Resins of average molecular weights of 5000-10000 have been found best for the present invention. These resins are commercially available in hard, brittle resin (No. 900) of melting point 180-190°C., tough flexible resins (No. 930 and 940) melting points 105-115°C., and in semi-solid, soft tacky resin (No. 100), melting point 43-55°C., and with some wax added (No. 950), which results in some turbidity in the final product. These resins are compatible with each other so that by blending them almost any desired properties in the aforesaid melting point range can be attained.

The tendency to syneresis of the oil-polyamide-cosolvent gels can be controlled

by use of amides having 12 to 18 carbon atoms in their molecules, for example diethanolamides fulfilling this condition and/or by curing the gels by holding them at temperatures between their melting point and the ambient temperature.

Hair treating gels are prepared by dissolving the polyamide resins in the hot organic system comprising the oily vehicle and the cosolvents (if included). Upon cooling, a gel structure is produced, and the properties will vary depending upon the amount of resin employed, the composition and molecular weight of the resin, and the compatibility and solubility of the resin in the vehicle chosen. The solubility of the polyamide resin in preferred solvent systems increases with temperature. Whenever the solubility limits of the polyamide resin in a particular solvent system are exceeded, a gel results which is thermally and mechanically reversible. Gels can be produced of a consistency from a soft jelly-like to a firm rigid structure, or of grainy, "crystal-like" structure or an amorphous, smooth glass-like structure.

Mixing at high temperatures, e.g. in the range 100-115°C may cause crystallization, whereas if the composition is mixed below 100°C and poured into moulds or jars at about 55°C and then kept for a substantial curing time, e.g. 1-6 days at an intermediate temperature, e.g. 37°C±2°C., a smoother structure and freedom from syneresis are attained. (See Example 9 below).

Such compositions are economical, thixotropic and less subject to syneresis than the brilliantine type compositions having a metal soap, such as aluminium stearate, as the gelling agent, in mineral oil.

It is an important advantage of the invention that crystal clear gels can be made, although opaque or cloudy gels are also within the broader scope of the invention. Such gels, whether crystal clear or non-clear, provide a thixotropic, non-greasy solid gel, which is liquefied quickly to a fluid by rubbing and is thus readily spread on and throughout the hair leaving the hair controlled and well groomed but with a natural soft appearance free from the "plastered-down" look and greasiness which have made most hair dressing compositions unacceptable to many persons.

Following are examples of compositions embodying the present invention which are suitable for hair grooming products:—

Examples of Gels	*% By Weight*
1. Clear tacky and substantially free of syneresis	
Polyamide 5000-8000 average MW	5.00
Castor Oil	95.00
	100.00
2. Simple system for clear gel:	
Polyamide 8000 average MW	5.00
Propylene glycol mono laurate	70.00
Light mineral oil	25.00
	100.00
3. Simple system for cloudy gel:	
Polyamide 8000 MW (average)	5.00
Propylene glycol mono laurate	47.50
Light mineral oil	47.50
	100.00
4. Simple system including large percentage of mineral oil (cloudy soft gel):	
Polyamide 8000 MW (average)	2.00
Oleic Acid	13.00
Light mineral oil	85.00
	100.00
5. Simple system for clear gel using a blend of polyamide resins:	
Polyamide 8000 MW (average)	2.50
Polyamide 5000 MW (average)	2.50
Propylene glycol mono laurate	70.00
Light mineral oil	25.00
	100.00

The light mineral oil referred to in this example is Marcol GX available from Esso Standard Oil Co. The use of other mineral oils in many systems produces hazy to cloudy gels. However, these other mineral oils can be made to give crystal clear systems by rebalancing the cosolvent fraction.

The gels of Examples 2 to 5 may be made by heating the oily solvent and the cosolvent to slightly above the melting point of the polyamide which is then introduced into the mixed solvents with agitation until the mass is homogeneous. The temperature is reduced to below 100°C and various additives are then introduced into the mass with stirring. It is then cured and filled into suitable containers.

A further improvement has been attained by using appropriate mixtures of cosolvents of the resin and mineral oil. This allows increase of the mineral oil content with corresponding decrease in cost, while preserving higher temperature stability and clarity of the gel:

Example 6 — A clear gel system using two cosolvents:

	Percentage by weight
Polyamide 8000 average MW	5.00
Propylene glycol mono laurate	19.10
Oleic Acid	10.90
Light mineral oil	64.00
Perfume	1.00
	100.00

by use of amides having 12 to 18 carbon atoms in their molecules, for example diethanolamides fulfilling this condition and/or by curing the gels by holding them at temperatures between their melting point and the ambient temperature.

Hair treating gels are prepared by dissolving the polyamide resins in the hot organic system comprising the oily vehicle and the cosolvents (if included). Upon cooling, a gel structure is produced, and the properties will vary depending upon the amount of resin employed, the composition and molecular weight of the resin, and the compatibility and solubility of the resin in the vehicle chosen. The solubility of the polyamide resin in preferred solvent systems increases with temperature. Whenever the solubility limits of the polyamide resin in a particular solvent system are exceeded, a gel results which is thermally and mechanically reversible. Gels can be produced of a consistency from a soft jelly-like to a firm rigid structure, or of grainy, "crystal-like" structure or an amorphous, smooth glass-like structure.

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Castor Oil	95.00
	100.00

2. Simple system for clear gel:		
Polyamide 8000 average MW	5.00	
Propylene glycol mono laurate	70.00	
Light mineral oil	25.00	
	100.00	70
3. Simple system for cloudy gel:		
Polyamide 8000 MW (average)	5.00	
Propylene glycol mono laurate	47.50	
Light mineral oil	47.50	75
	100.00	
4. Simple system including large percentage of mineral oil (cloudy soft gel):		80
Polyamide 8000 MW (average)	2.00	
Oleic Acid	13.00	
Light mineral oil	85.00	
	100.00	85
5. Simple system for clear gel using a blend of polyamide resins:		
Polyamide 8000 MW (average)	2.50	
Polyamide 5000 MW (average)	2.50	90
Propylene glycol mono laurate	70.00	
Light mineral oil	25.00	
	100.00	

The light mineral oil referred to in this example is Marcol GX available from Esso Standard Oil Co. The use of other mineral oils in many systems produces hazy to cloudy gels. However, these other mineral oils can be made to give crystal clear systems by rebalancing the cosolvent fraction.

The gels of Examples 2 to 5 may be made by heating the oily solvent and the cosolvent to slightly above the melting point of the polyamide which is then introduced into the mixed solvents with agitation until the mass is homogeneous. The temperature is reduced to below 100°C and various additives are then introduced into the mass with stirring. It is then cured and filled into suitable containers.

A further improvement has been attained by using appropriate mixtures of cosolvents of the resin and mineral oil. This allows increase of the mineral oil content with corresponding decrease in cost, while preserving higher temperature stability and clarity of the gel:

Example 6 — A clear gel system using two cosolvents:

	Percentage by weight
Polyamide 8000 average MW	5.00
Propylene glycol mono laurate	19.10
Oleic Acid	10.90
Light mineral oil	64.00
Perfume	1.00
	100.00

The mineral oil can be used in an amount from 1-80% by weight of the gel, and the polyamide in an amount from 1-40% by weight, (advantageously 2-10% by weight) but in general the use of higher proportions of oil leads to some deterioration of the gel structure and its thermal stability. If the product is subjected to long storage at ambient temperatures, or higher, even the compositions made as above may show some tendency to syneresis. When any separation becomes evident, even though the product still preserves its excellent hair grooming properties, the customer may assume that it is "spoiled." In such cases, special precautions should be taken.

This problem can be controlled and a gelled thixotropic hair groom composition which does not break down or separate, even after long periods of storage at ambient temperatures, can be provided. This is attained by including in the composition as a stabilizer, an amide having a chain of at least 10 carbon atoms in its molecule. The following amides are advantageous as stabilisers:—

Lauryl diethanolamide
Stearyl diethanolamide
Oleyl diethanolamide
Lauryl diethanolamide-Ethoxylated Nonyl Phenol Adduct
Linoleyl diethanolamide
Coconut oil fatty acids diethanolamide
Coconut oil diethanolamide
Tallow fatty acid diethanolamide
Soy bean fatty acid diethanolamide

Kritchevsky Condensates such as:—

Coconut Oil-Diethanolamine Condensate and
Lauric Acid-Diethanolamine Condensate.

(Kritchevsky Condensates are products of the condensation of polyalkylol amines with fatty acids or glycerides thereof, said acids having 12-14 carbon atoms in their molecules).

As an illustration of the manner of using such stabilisers the following example is given:

Example 7 — Stabilised clear gel systems (at ambient temperatures, uncured)

	% *By Weight*
Polyamide 8000 average MW	5.00
Propylene glycol mono laurate	13.40
Lauryl diethanolamide	5.70
Oleic acid	10.90
Light mineral oil	64.00
Perfume	1.00
	100.00

Protection against syneresis can be gained or extended by curing the gel at a constant temperature between the melting point of the gel and ambient temperature. After such curing our gelled compositions are protected against syneresis at considerably higher temperatures.

The combination of the polyamide resin and oil with cosolvent can also be used for its extraordinary hair grooming and fixative effect in other than gel form. Examples of such are:

Example 8—Spray Aerosol	% *By Weight*	
Polyamide 8000 average MW	5.00	
Ethyl alcohol (specially denatured alcohol No. 40 anhydrous)	80.00	35%
Lanolin oil	1.00	
Propylene glycol mono laurate	13.40	
Perfume	0.60	
Propellant 11 (Trichloro mono-fluoro methane)	50.00	65%
Propellant 12 (Dichloro di-fluoro methane)	50.00	
	100%	

The above is an example of the case mentioned previously where propylene glycol mono-laurate acts as the liquid, oily non-polar solvent rather than as a cosolvent. Instead of lanolin oil, other lanolin derivatives which are compatible with the system may be used.

Example 9 — Clear Liquid Brilliantine

Thixotropic Liquid type	% *By Weight*
Polyamide 8000 average MW	5.00
Propylene glycol mono laurate	84.00
Light mineral oil	10.00
Perfume	1.00
Free Flowing Liquid type	
Polyamide 8000 average MW	5.00
Oleic Acid	84.00
Light mineral oil	10.00
Perfume	1.00

Example No. 10 — Alcoholic Liquid Hair Groom

	Parts by Weight
Polyamide 8000 average MW	2.00
Light mineral oil	43.70
Propylene glycol mono laurate	14.00
Oleic Acid	7.30
Ethyl alcohol (specially denatured alcohol No. 40. anhydrous)	32.00
Perfume	1.00

Example 11 — Emulsified Cream Hair Groom

Polyamide 8000 average MW	5.00
Propylene glycol mono laurate	15.00
Stearic acid	10.00
Triethanolamine	2.00
Water	67.00
Perfume	1.00

In the above example, propylene glycol mono laurate again constitutes the liquid,

oily, non-polar solvent as in Example 8.

The above emulsion is an example of an anionic type system. To those skilled in the art of emulsion making, it is readily understood that similar systems can be produced using non-ionic and cationic emulsifiers or combinations of both.

The use of the above formulations, comprising the polyamide resin together with the other ingredients, results in more enhanced hair grooming efficiency and produces a greater brilliance than that obtained with formulations of the conventional type.

Hair grooming properties of polyamides in gel systems were substantiated by half-head experiments, as described below:—

A gob of a clear gel about the size of a finger nail was weighed and liquefied by rubbing in the palm of the hand and applied to hair on half of one's head. An equivalent weight of the same formulation, but without the polyamide contained therein, was applied to the other half of the same head. Both halves were combed identically and the halves were compared for brilliance, grooming qualities, and hair fixative properties. The results indicated that the half-head containing the polyamide was superior in the aforementioned qualities. The preceding test was more demonstrative when hair switches of identical hair were used in place of the half-heads.

It should be recognised that in addition to improving hair grooming properties, the use of the polyamide resins, as a gelling agent for solid brilliantines, is also new.

WHAT WE CLAIM IS:

1. A hair grooming composition comprising a polyamide material at least partly dissolved in a liquid, oily, non-polar solvent consisting of or including a substance having a chain of at least 10 carbon atoms in its molecule, the polyamide material being a reaction product of an aliphatic polycarboxylic acid and an alkylene polyamine and having an average molecular weight between 2000 and 14000.

2. A hair grooming composition as claimed in claim 1 in which the polyamide material is solid at ambient temperatures.

3. A hair grooming composition as claimed in claim 2 including a cosolvent which forms with the polyamide a solution which is miscible with the liquid, oily solvent.

4. A hair grooming composition as claimed in claim 2 or 3 in which the liquid, oily solvent has a viscosity between 50 and 70 Saybolt.

5. A hair grooming composition as claimed in claim 2, 3 or 4 which contains from 1% to 40% by weight of the polyamide material and from 1% to 80% by weight of the liquid oily solvent.

6. A hair grooming composition as claimed in claim 2, 3, 4 or 5 which contains from 2% to 10% by weight of the polyamide material.

7. A hair grooming composition as claimed in any of the claims 2 to 6 in which there is incorporated a stabiliser which is an amide having a chain of at least 10 carbon atoms in its molecule.

8. A hair grooming composition as claimed in claim 7 and which has been cured at a temperature between the melting point of the composition and ambient temperature.

9. A hair grooming composition as claimed in any one of claims 2 to 8 in which the said polycarboxylic acid is polymerized linoleic acid.

10. A hair grooming composition as claimed in any one of claims 2 to 9 in which the average molecular weight of the polyamide material is from 5000 to 10000.

11. A hair grooming composition as claimed in claim 7 or 8 in which the said stabiliser is a diethanolamide having 12 to 18 carbon atoms in its molecule.

12. A hair grooming composition as claimed in any one of the preceding claims including a perfume.

13. A method of grooming hair comprising the step of applying a hair grooming composition according to any one of the preceding claims to the hair.

14. A method of preparing a hair grooming composition according to claim 1 comprising the steps of forming a mixture of the polyamide material in the oily liquid non-polar solvent, and at least partially dissolving said polyamide in the solvent by applying heat to said solvent either before or after addition of said polyamide.

15. A hair grooming composition substantially as described in any one of the examples hereinbefore set forth.

16. A method of preparing a hair grooming composition substantially as hereinbefore described.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1968.
Published at the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.